syn- and *anti*-Benzotris(norbornadiene)s

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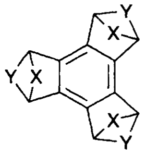
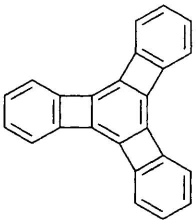
The hitherto unknown *syn* and *anti* isomers of benzotris(norbornadiene) 7, the only molecules that include both features known to lead to bond length alternation in benzenes, *i.e.* bicyclic ring strain and π–π interaction, have been synthesized from 2,3-dibromonorbornadiene using butyllithium and copper(I) iodide.

Trisannelated polycyclic molecules such as **1**–**6** are enjoying widespread interest as molecules where the bond length alternation within the benzene unit, as originally postulated by Mills and Nixon, can be experienced.[1] Although bond length alternation is rarely observed and the Mills–Nixon effect is questioned,[7] there is no doubt as to the radialenic-type structure in fullerenes and thus, there is a need to enlarge this class of molecules to gain a deeper insight into the question. In this regard, the benzotris(norbornadiene)s **7**[†] are amongst the most significant representatives of this class, because they are the only molecules that include both features so far known to induce bond length alternation in benzenes,[8] *i.e.* the bicyclic ring strain maximized in **1**[9] and the π–π interaction as in [3]phenylene **6**.[10] Indeed, the structures of *syn*- and *anti*-**7**, optimized *ab initio* at the 3-21G* level,[‡] show a bond length of 1.434 Å for the endocyclic benzene bond and 1.343 Å for the exocyclic bond. A difference of 0.091 Å between the benzene bonds for **7** shows that it possesses a highly distorted benzene ring. In addition to this, molecules such as **7** should exhibit unusual redox properties and, especially the *syn* isomer, interesting complexing features with a number of metals. In our own area of research, *syn*- and *anti*-**7** represent the starting materials for the preparation of non-planar polycondensed aromatic hydrocarbons.

From the outset, the method used in the synthesis of the closest member of the series, *i.e.* the oxa-analogue **4**,[5] is not valid for **7**, as it requires strongly basic conditions for the generation of a benzyne precursor, compatible with furan, but not with cyclopentadiene. Rather, *syn*- and *anti*-**7** were obtained as an almost statistical mixture of isomers (1 : 2.6) in 10% yield, *via* cyclotrimerization of 2,3-dibromonorbornadiene **8**[11] with butyllithium and copper(I) iodide using a method resembling the original procedure Gassman used for the synthesis of **2**.[3,4] The two isomers appear quite similar in their physical and chemical properties, so that no clear separation was ever achieved by GC or HPLC, despite using different columns and conditions. Numerous attempts to effect separation *via* fractional crystallization were unsuccessful, a technique that is successfully reported for the separation of similar compounds such as **2** and **3**. The GC–MS spectrum performed on the mixture of *syn*- and *anti*-**7** shows the correct molecular ion peak at *m*/*z* 271 ($M^{+} + 1$), suggesting the correct C, H composition which was confirmed by microanalysis. The structure of *syn*- and *anti*-**7** was, however, fully elucidated by a thorough NMR spectroscopic study at 400 MHz. Both the proton and carbon NMR spectra of the two isomers could be convincingly identified, allowing a clear distinction between the resonances belonging to the two isomers.[§] Analysis of the vinylic region of the spectrum was decisive in the structural assignment. Two pseudo triplets at δ 6.69 and 6.56 are the AA′ portions of two AA′XX′ second order systems, describing the vinyl and bridgehead protons of symmetric norbornenyl skeletons. Two doublets of doublets at δ 6.66 and 6.59 are the A and B vinyl protons of an ABXY system describing the vinyl and bridgehead protons of an asymmetric norbornenyl skeleton. In agreement with this assignment, the decoupling of the bridgehead protons, which resonate undifferentiated at about δ 3.87, reduces the pseudo triplets to singlets, and the two doublets of doublets to two doublets. Accurate integrations of these resonances show that the ratio of the AA′ protons at δ 6.69 to the AB protons is 1 : 2. It is therefore straightforward to attribute these resonances to the asymmetric structure *anti*-**7**, where the A and B vinyl protons are differentiated by the opposing orientations of the flanking norbornenyl rings. The AA′ protons at δ 6.56 have an integral ratio with the cumulated integrals of the other vinyl resonances of 1 : 2.6. This resonance is assigned to the vinyl protons of the symmetric structure *syn*-**7**. The two isomers *syn*- and *anti*-**7**, in an approximate 1 : 2.6 ratio, should give rise to four vinyl and four aromatic ^{13}C resonances, which have been detected in two narrow regions (δ 141.7–142.1 and 137.6–138.2, respectively). Significant multiple bond ^{1}H–^{13}C correlations have been detected by HMBC spectroscopy (multiple bond HMQC spectroscopy)[12] between the ^{1}H resonances of apical protons in the δ 1.98–2.10 region and the four vinyl ^{13}C resonances, and between the apical proton resonances in the δ 2.15–2.24 region and the four aromatic ^{13}C resonances. According to the Karplus curve for $^{3}J_{\mathrm{C,H}}$ constants,[13] the



1 X = Y = CH_2 (ref. 2)
2 X = CH_2, Y = CH_2CH_2 (ref. 3)
3 X = Y = CH_2CH_2 (ref. 4)
4 X = O, Y = CH=CH (ref. 5)
5 X = Y = C_6H_4 (ref. 6)



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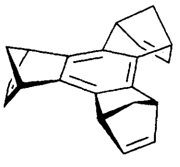
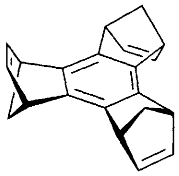
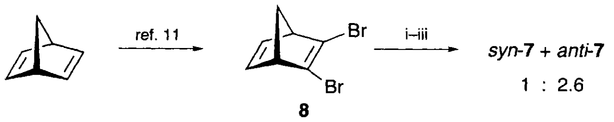


syn-**7**



anti-**7**



Scheme 1 *Reagents and conditions*: i, BuLi, −78 °C, 1 h; ii, CuI, −50 °C, 1 h; iii, room temp., 12 h, 10%

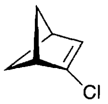
resonances in the δ 1.98–2.10 region are assigned to the apical protons *syn* to the aromatic ring and those in the δ 2.15–2.24 region are assigned to the *anti* protons. The low resolution of the HMQC spectrum does not allow the assignment of the single ^{13}C resonances. However, accurate integration of the ^{13}C signals in spectra recorded with gated ^{1}H decoupling, and the fact that the product ratio differs from the statistical 1 : 3 ratio, allows the assignment of the two isomers.

From the synthetic point of view it should be noted that the use of other salts[14] as well as nickelocene, which are effective in the cyclotrimerization of the related 2,3-dibromonorbornene to give **2**,[3] proved ineffective for **7**, giving only polymers.

Other possible methods for the synthesis of *syn*- and *anti*-**7** also failed. For example, while cyclotrimerization of 2-chloroderivatives **9** and **10** with butyllithium is successful for the synthesis of **1**[2] and **2**,[3] it is not with 2-chloronorbornadiene **11**.

Reasoning that the major cause of polymerization might be due to the presence of the extra double bond, compound **12**, with the double bond protected as a ketal, was synthesised. Starting from norbornenone, compound **12** was obtained by the reaction sequence shown in Scheme 2 in very good overall yield. Unexpectedly, however, it gives, under the reaction conditions which are successful for the preparation of **2**, the dimers **13** and **14**, whose structures were characterised by diffractometric analyses. Other attempts to prepare **7** with reagents and strategies successfully employed for the synthesis of **1**–**6** also failed.[15]

The unfortunate discovery that the two isomers *syn*- and *anti*-**7** cannot be separated and our inability to grow crystals suitable for X-ray crystallographic structure analysis, prevent us from thoroughly defining the cyclohexatrienic character of *syn*- and *anti*-**7**. Work is currently in progress aimed at devising new methods for the synthesis of benzoannelated trimers that will hopefully allow us to obtain larger quantities of these molecules, both for a more thorough study of their chemical and electronic properties, and to allow the synthesis of non-planar polycondensed aromatic hydrocarbons related to the fullerenes.



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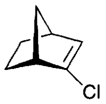

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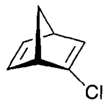

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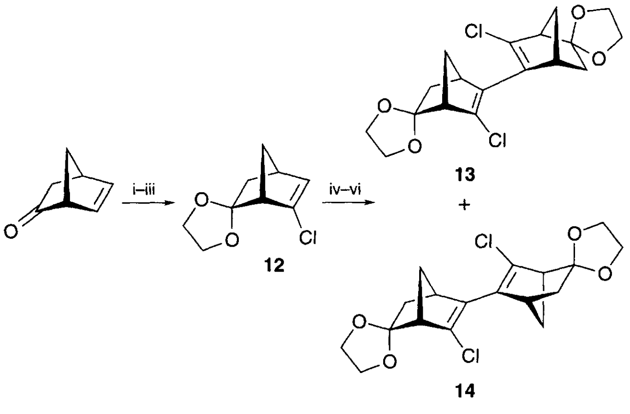

Scheme 2 *Reagents and conditions*: i, PhSeCl (1 equiv.), $CHCl_3$, room temp., quant.; ii, $NaIO_4$, $NaHCO_3$, MeOH, H_2O, room temp., 3 h, 95%; iii, $HOCH_2CH_2OH$, TsOH, PhH, reflux, 2 h, 98%; iv, Bu^{t}Li, −78 °C, 1 h; v, CuI, −45 °C, 1 h; vi, room temp., 12 h, 60% from **12**

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Footnotes

† The structures of *syn*- and *anti*-**7** are drawn on the basis of MM2 parameters.

‡ SPARTAN program package, ver. 4.0, distributed by Wavefunction, Inc., 18401 Von Karman Ave., Irvine, CA 92715 USA.

§ Inseparable mixture of the *syn* and *anti* isomers in a 1 : 2.6 ratio by silica gel column chromatography (eluant hexane), mp 198–207 °C (hexane). *Selected data* for *syn*-**7**; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.57 (t, *J* 2.0 Hz, 6 H), 3.90–3.87 (m, 6 H), 2.22 (dt, 1/2 AB system, *J* 7.1, 1.6 Hz, 3 H), 2.08 (dt, 1/2 AB system, *J* 7.1, 1.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.99 (d), 137.79 (s), 66.73 (t), 47.41 (d). For *anti*-**7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.68 (t, *J* 1.8 Hz, 2 H), 6.65 (dd, *J* 8.0, 3.0 Hz, 2 H), 6.59 (dd, *J* 8.0, 3.0 Hz, 2 H), 3.90–3.87 (m, 2 H), 3.87–3.85 (m, 4 H), 2.05 (dt, 1/2 AB system, *J* 7.1, 1.6 Hz, 4 H), 2.00 (dt, 1/2 AB system, *J* 7.1, 1.6 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.13 (d), 141.80 (d), 141.71 (d), 138.18 (s), 137.85 (s), 137.64 (s), 66.60 (t), 66.39 (t), 47.43 (d), 47.38 (d), 47.37 (d); IR (KBr disk, 1 : 2.6 mixture of *syn*- and *anti*-**7**) 2966, 2934, 2868, 1564, 1453, 1354, 1301, 734 cm^{-1}; m/z (70 eV) 271 (M^+ + 1), 270 (base peak), 255, 243, 239, 229, 215, 202, 189, 187, 176, 165, 152, 126, 120, 113, 101, 87, 75, 63.

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